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Alcohol promoted methanol synthesis enhanced by adsorption of water and dual catalysts

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1 **Alcohol promoted methanol synthesis enhanced by adsorption of water and dual catalysts**

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6 **Abstract**

7 Alcohol-promoted methanol synthesis uses heterogeneous methanol synthesis catalysts in alcoholic solvents

8 where the alcohols act as a co-catalyst. In the presence of alcohol, the reaction proceeds through alcohol formate

9 ester as an intermediate, allowing methanol synthesis at lower temperatures than conventional gas-phase

10 synthesis. In the present work, alcohol-promoted CO_2 hydrogenation to methanol was studied experimentally using

11 a Cu/ZnO catalyst with 1-butanol and 2-butanol as solvents. As water is known to inhibit methanol synthesis on

12 Cu/ZnO catalysts, the alcohol-promoted process was further developed by in-situ adsorption of water using a 3Å

13 molecular sieve. The methanol productivity significantly improved as a result of the lowered concentration of water.

14 The concentration of water was thus identified as a key factor affecting the overall methanol productivity. As the

15 alcohol-promoted methanol synthesis process is characterized by two separate reaction steps, the use of separate

16 catalysts optimized for each step offers an interesting approach for the development of this process. Such a dual-

17 catalysis concept was tested using a copper chromite catalyst together with Cu/ZnO. Promising results were

18 obtained, as methanol productivity increased with the addition of copper chromite. Catalyst characterization was

19 carried out using XRD and SEM-EDS and potential effects of observed changes in catalyst structure during reaction

20 are discussed.

21 **Keywords**

22 CO_2 hydrogenation, methanol synthesis, Cu/ZnO, liquid-phase, alcohol promoted, dual catalysis, copper chromite,

23 molecular sieve

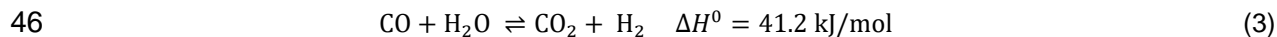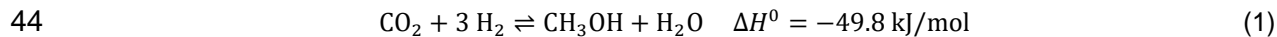24 **Conflicts of interest**: none

25

1. Introduction

Development of efficient and flexible energy storage methods is critical for a global shift from a fossil fuels based economy to a renewable energy based economy [1]. The use of surplus peak electricity generated from fluctuating renewable energy sources, such as wind and solar energy, for the production of chemical compounds would enable energy storage in a highly transportable form at high energy density. Generation of hydrogen by electrolysis of water is the common starting point in chemical energy storage strategies [2]. However, due to the difficulties and hazards associated with large-scale storage and transportation of gaseous hydrogen, further utilization of hydrogen for production of carbon-containing liquid fuels and chemical compounds might be preferable.

Methanol is an example of such a potential liquid-phase chemical energy carrier [3]. Methanol is an important and versatile industrial chemical that can also be used as a fuel in power generation and in internal combustion engines and fuel cells [4]. Additionally, methanol is a versatile raw material for synthesis of a variety of chemical products. For instance, methanol can be transformed into gasoline in the methanol-to-gasoline process (MTG) [5] or into olefins in the methanol-to-olefins process (MTO) [6].

Current production of methanol is based on catalytic conversion of synthesis gas generated from fossil sources, commonly natural gas. The syngas is mainly composed of mixtures of hydrogen, carbon monoxide and carbon dioxide. In conventional methanol synthesis, copper and zinc oxide (Cu/ZnO) catalysts are generally employed at reaction temperatures of 200-300 °C and pressures of 50-100 bar [7].

The methanol synthesis process can be described by the following three equilibrium reactions:

$$CO_2 + 3\ H_2 \rightleftharpoons CH_3OH + H_2O \quad \Delta H^0 = -49.8\ kJ/mol \tag{1}$$

$$CO + 2\ H_2 \rightleftharpoons CH_3OH \quad \Delta H^0 = -91.0\ kJ/mol \tag{2}$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad \Delta H^0 = 41.2\ kJ/mol \tag{3}$$

The exothermic reactions (1) and (2) represent, respectively, the hydrogenation of CO_2 and CO to methanol. Reaction (3), the water-gas shift (WGS) reaction, is relevant to methanol synthesis as the reaction is also activated by the copper-based methanol synthesis catalysts [8]. As methanol synthesis is exothermic and results in a reduction of molar volume, methanol synthesis is favored by low temperatures and high pressures. However,

51   temperatures above 200 °C are required for sufficiently high reaction rates, and thus the thermodynamic equilibrium

52   limits the methanol synthesis to low conversion levels. Hydrogenation of pure CO_2 to methanol is also possible but

53   the equilibrium conversions are even lower than for CO. Figure 1 shows the calculated equilibrium conversion of

54   stoichiometric CO and CO_2 feeds at different temperatures and pressure. The conversions are modelled by Soave-

55   Redlich-Kwong equations of state, which have been shown to accurately predict experimental results in methanol

56   synthesis [9]. However, the hydrogenation of CO_2 on Cu/ZnO catalysts is highly selective to methanol, with other

57   thermodynamically more favorable products such as methane, ethers and ketones formed only in negligible

58   amounts [10].

CO$_2$, 40 bar   CO$_2$, 100 bar
CO, 40 bar   CO, 100 bar
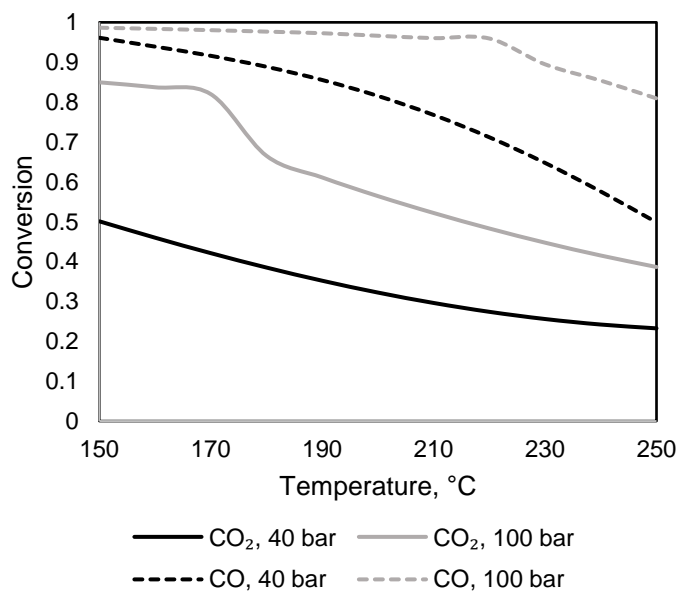
59

60   **Figure 1.**   Effect of temperature and pressure on the equilibrium carbon conversion from stoichiometric

61   CO_2:H_2 (1:3) and CO:H_2 (1:2) mixtures. Calculated with the predictive Soave-Redlich-Kwong

62   (PSRK) [11] equation of state in Aspen Plus.

63   To overcome the thermodynamic limitations in the gas-phase methanol process, liquid-phase synthesis processes

64   have been proposed as an alternative approach to enable lower reaction temperatures in syngas reactions. Early

65   developments utilized highly basic catalyst systems such as alkali alkoxides in combination with copper chromite

66   [12, 13, 14] or nickel-based catalysts [15, 16, 17]. Methanol synthesis from CO/H_2 at temperatures as low as 100

67   °C and pressures between 30 and 65 bar were reported [18]. However, the basic catalysts are incompatible with

68   CO_2 or water, the presence of which, even at trace amounts, leads to rapid catalyst deactivation [17]. A method

69   proposed by the Brookhaven National Laboratory (BNL) also utilized a highly basic system for the conversion of

70   CO to methanol at significantly low temperature and pressure [19]. Furthermore, liquid-phase methanol synthesis

71   from CO_2-containing synthesis gas in inert hydrocarbon solvent has been demonstrated in the LPMeOH process

72   [20].

73   CO_2 has been identified as the main carbon source in methanol synthesis from syngas [21]. Hence, it may be

74   expected that methanol can also be produced by hydrogenation of pure CO_2. Hydrogenation of CO_2, captured from

75   point sources or even directly from the atmosphere, would then provide a sustainable source of carbon-based fuels

76   and chemicals while helping to reduce the atmospheric concentration of CO_2 [22]. Some pilot-scale methanol

77   processes that can use CO_2 as the starting material have been developed. These include the CAMERE process

78   [23], which combines the reverse water-gas-shift reaction and methanol synthesis from syngas, and the Matsui

79   Chemicals process [24], which directly converts CO_2 to methanol. Additionally, Carbon Recycling International

80   established commercial methanol production from CO_2 in 2011, and the Svartsengi plant is presently operating at

81   a capacity of above 5 million liters per year [25]. The process utilizes geothermal energy readily available in Iceland.

82   One possible way to influence the reaction kinetics and conditions is to change the reaction route that leads to the

83   formation of methanol. A novel alcohol-promoted liquid-phase methanol synthesis process first proposed by Fan et

84   al. [26] is based on the combination of a conventional Cu/ZnO catalyst and alcohol as a catalytic solvent. The

85   alcohol promotes methanol synthesis by altering the reaction route, allowing operation at lower temperatures. In

86   the presence of the alcohol, the reaction proceeds through the formate ester of the corresponding alcohol as an

87   intermediate. As a result, methanol can be produced from syngas at temperatures starting from 170 °C and

88   pressures in the range of 30 to 50 bar [27]. Importantly, the process does not employ basic catalysts sensitive to

89   deactivation by CO_2, allowing direct conversion of CO_2. The following reaction steps have been proposed for this

90   process [28], supported by subsequent *in-situ* IR observations [29]:

91   1. Hydrogenation of carbon dioxide into formic acid

92                    $$CO_2 + H_2 \rightleftarrows HCOOH \tag{4}$$

93

94   2. Reaction of formic acid with ethanol, forming ethyl formate

95

96      $$HCOOH + C_2H_5OH \rightleftarrows HCOOC_2H_5 + H_2O \qquad (5)$$

97

98   3. Hydrogenation of ethyl formate, forming methanol and ethanol

99      $$HCOOC_2H_5 + 2\,H_2 \rightleftarrows CH_3OH + C_2H_5OH \qquad (6)$$

100 The net reaction is the hydrogenation of carbon dioxide to methanol (Eq. 1) with a standard reaction enthalpy of -

101 49.8 kJ/mol. Different alcohols have been shown to possess different promoting effect for methanol synthesis.

102 Tsubaki et al. [30] found linear alcohols to be more effective compared to their branched counterparts, with n-

103 butanol showing the best results. Zeng et al. [31] reported that the yield of both methanol and the corresponding

104 ester decreased with increasing carbon number of the 1-alcohols from ethanol to 1-hexanol. For alcohols with the

105 same carbon number but different structure, 2-alcohols were found to have higher activity, which was explained by

106 a combination of spatial and electronic effects. As a result, 2-propanol showed the highest promotional effect. Later,

107 2-butanol was reported as the most effective solvent for the continuous methanol synthesis in a semibatch reactor

108 [32].

109 As the alcohol-promoted methanol synthesis process is characterized by two separate reaction steps, the utilization

110 of separate catalysts optimized for each reaction could be beneficial. Such dual- or cascade catalytic systems have

111 been considered previously for methanol synthesis. Huff and Sanford [33] reported effective CO_2 conversion to

112 methanol at 135 °C using a combination of homogeneous catalysts. Chen et al. [34] used heterogeneous catalysts

113 in 1,4-dioxane solvent: copper chromite for the hydrogenation of CO_2 to formate and Cu/Mo_2C for the formate

114 hydrogenolysis to methanol. This system was capable of methanol production at rates comparable to conventional

115 gas-phase synthesis at 135 °C and exhibited methanol selectivity above 75%. The methanol synthesis was

116 promoted by the addition of ethanol, with the reaction proceeding through ethyl formate, as reported in the alcohol-

117 promoted process. On the other hand, copper chromite is known to catalyze the hydrogenolysis of esters to

118 alcohols, i.e. the latter stage in the alcohol-promoted reaction route [35]. As such, copper chromite appears an

119 interesting component of a dual catalytic system for alcohol-promoted methanol synthesis.

120 In comparison to CO-containing syngas feed, CO_2 hydrogenation to methanol is further complicated by the

121 increased formation rate of water. Water is formed as a byproduct in methanol synthesis, and in the absence of

122 CO, the water-gas shift reaction proceeds in the reverse direction, producing more water. The negative effect of

123 water on methanol synthesis on Cu/ZnO-based catalysts has been well documented [36]. This effect has been

124 explained as a combination of kinetic inhibition effects and structural catalyst deactivation. Water-derived hydroxyl

125 species can block the active sites on the catalyst, resulting in kinetic inhibition. The presence of water can also

126 accelerate the sintering of copper particles [37], resulting in decreased copper dispersion and catalyst deactivation.

127 Removal of methanol and water using membrane reactors [38, 39] and by condensation at high pressures [40] or

128 low temperatures [41] has been previously described for gas-phase methanol synthesis. Reactive distillation [42]

129 provides a further possible approach for continuous product removal, particularly in liquid-phase processes, and

130 has been proposed in literature for the methanol synthesis process [43] and for the Fischer-Tropsch process [44]

131 operating at similar conditions. In addition, selective removal of water by adsorption on zeolite molecular sieves has

132 also been suggested in sorption-enhanced methanol [45] and related dimethyl ether [46] synthesis operated in the

133 gas-phase.

134 In the present work, alcohol-promoted methanol synthesis was investigated experimentally using a commercial

135 Cu/ZnO-based methanol synthesis catalyst with 1-butanol and 2-butanol as the solvents. 2-butanol was selected

136 because of the previously reported high activity for methanol synthesis, and 1-butanol was considered interesting

137 because of the potentially simplified product separation due to the higher boiling point of the alcohol. As novel

138 developments, enhancement of the alcohol-promoted methanol synthesis by *in-situ* adsorption of water and by the

139 use of dual catalysts were studied. Water adsorption was carried out using a molecular sieve. Methanol synthesis

140 combined with water removal has previously been modelled based on 4Å molecular sieves [45], and the use of 4Å

141 molecular sieves has been modelled for a related dimethyl ether (DME) synthesis [46]. However, experimental work

142 of methanol synthesis promoted by water adsorption has not been published earlier to our knowledge. A dual

143 catalyst system comprising of a combination of Cu/ZnO and copper chromite catalysts was tested with the aim of

144 improving methanol productivity by influencing separately the formate formation and hydrogenolysis reaction steps.

145 **2. Materials and methods**

146 A Parr 4520 autoclave reactor with an inner volume of 450 ml was used for the reaction experiments. The reactor

147 was connected to a Parr 4848 control unit used to control the reaction temperature and mixing speed. A mixing

148 speed of 600 rpm was used in all experiments. Liquid samples from the reaction mixture were collected using a

149 water-cooled sample collection vessel, in which any vapors present in the sample were condensed prior to collecting

150 the sample.

151 Analysis grade 1-butanol and 2-butanol, were used as solvents. A commercial Cu/ZnO-based methanol synthesis

152 catalyst (Alfa Aesar, 65.5 % CuO, 24.7% ZnO, 10.1% Al_2O_3, 1.3% MgO) was used. The catalyst was ground and

153 sieved to 150-500 μm for each experiment. The 3Å molecular sieve (UOP, beads with diameter of 2 mm), was also

154 ground and sieved to 150-500 μm. An initial experiment with the unground molecular sieve was also performed.

155 The molecular sieve was activated by heating to 250 °C for at least 8 hours under air and subsequent cooling to

156 ambient temperature inside a desiccator prior to use. Powdered copper chromite (Sigma-Aldrich) was used in the

157 dual catalyst experiments. A mixed gas containing 75% hydrogen and 25% carbon dioxide was used as the reaction

158 feed gas, and a mixed gas containing 5% hydrogen in nitrogen was used for activation of the catalysts. A diagram

159 of the experimental setup is presented in Figure 2.
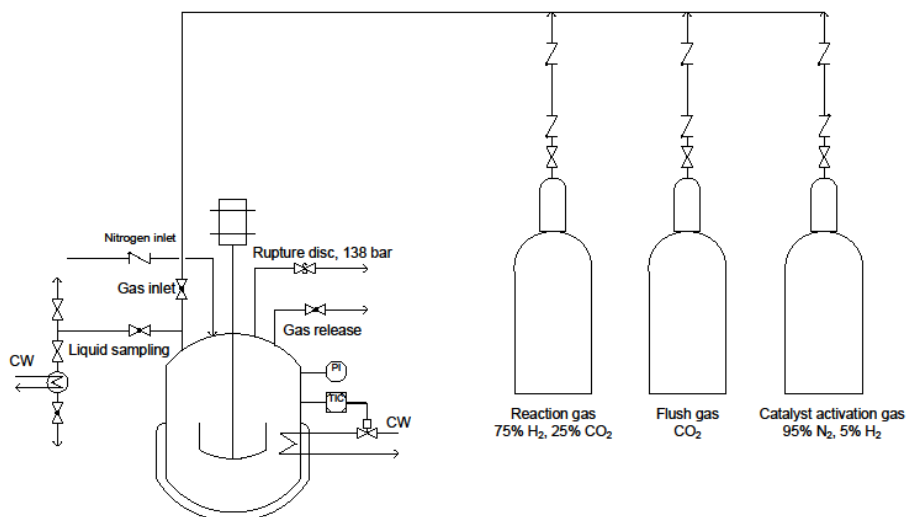
160

161 **Figure 2.** Experimental setup used in the reaction experiments.

162 The ground Cu/ZnO catalyst and the copper chromite catalyst were activated *in-situ* in the reactor vessel. Catalyst

163 activation was performed under 5 bar of the 5% H_2/N_2 mixed gas, with the gas inside the reactor replaced every 30

164 minutes. The temperature was 200 °C during the activation. Following catalyst activation, the reactor was cooled

165 and the catalysts were kept under the activation gas until the reaction experiment was executed. 200 ml of the

166 alcohol was quickly poured into the reactor, minimizing the contact time of the catalysts with air. The reactor was

167 purged with nitrogen and heated to the reaction temperature under N_2. At the reaction temperature, an initial liquid

168 sample was collected and the reactor was pressurized with the feed gas (CO_2:H_2 = 1:3) to the set reaction pressure,

169 which was 60 bar unless otherwise noted. Constant pressure was maintained during the experiments by replacing

170 the consumed reaction gas with fresh gas. The total reaction time was 6 hours and liquid samples were collected

171 every 2 hours.

172 An Agilent Technologies 6890N gas chromatograph with a thermal conductivity detector was used for analysis of

173 the liquid samples. A polar Zebron ZB-WAXplus column was used for the 2-butanol samples. An isothermal method

174 with the column temperature at 70 °C and helium (1.1 ml/min) as a carrier gas was used. For the 1-butanol samples,

175 a non-polar HP-1ms column was used due to insufficient separation of butanal and methanol in the ZB-WAXplus

176   column. A temperature program with an initial temperature of 50 °C (3 minute hold) followed by a 25 °C/min ramp

177   to 100 °C (3 minute hold) was used. Helium (0.7 ml/min) was used as the carrier gas. In the ZB-WAXplus column,

178   the retention times were 2.9 min for methanol, 3.0 min for 2-butanone, 3.8 min for 2-butanol, and 3.9 min for water.

179   In the HP-1ms column, the retention times were 2.7 min for water, 2.9 min for methanol, 4.7 min for butanal, and

180   5.8 min for 1-butanol. Sample concentrations were calculated by the external standard method.

181   Analysis uncertainty was estimated by repeated measurements and by estimation of the uncertainty related to the

182   preparation and analysis of the calibration standards. The total uncertainty is expressed as the relative standard

183   deviation for each product compound in 1-butanol and 2-butanol, which is presented as error bars in the relevant

184   figures. In 1-butanol, the relative standard uncertainty is 8% for methanol, 11% for water and 12 % for butanal. In

185   2-butanol, the relative standard uncertainty is 8% for methanol and 11% for water. The uncertainty related to the

186   experimental procedure was estimated as relatively insignificant.

187   Characterization of the Cu/ZnO catalyst by XRD and SEM-EDS was performed in order to observe any structural

188   changes in the catalyst during the reaction. The catalyst used in methanol synthesis in 1-butanol at 180 °C was

189   analyzed before the reaction (in calcined form) following grinding, and also after the experiment. A separate batch

190   of ground catalyst was characterized by XRD following reduction by the method described above.

191   XRD analysis was performed on a Bruker D8 Advance system with Cu-Kα radiation at 2θ of 20° to 90° at 0.02°

192   increment, with fixed sample illumination and LYNXEYE 1D detector. For analysis, a layer of the ground catalyst in

193   the 150-500 μm particle size range was placed on the plastic powder specimen holder, which was rotated at 10

194   rpm during analysis. Phase analysis was performed in DIFFRAC.SUITE EVA software based on the PDF 4+ 2018

195   database. SEM micrographs and EDS element analyses were obtained using a Hitachi SU3500 Scanning Electron

196   Microscope with SE detector and Thermo Fisher Scientific UltraDry SDD EDS. The acceleration voltage was varied

197   between 10 and 20 kV. The samples were introduced as 150-500 μm particles on a two-sided carbon tape, without

198   coating.

199   **3. Results and discussion**

200   **3.1 Detected reaction products**

201   In addition to methanol and water, significant quantities of alcohol dehydrogenation products were found in the

202   reaction mixture. Alcohol dehydrogenation is known to be catalyzed by copper catalysts [47] with the reaction

203   yielding corresponding aldehydes or ketones and hydrogen as products [48]. For instance, the dehydrogenation of

204   1-butanol yields butanal, while 2-butanol is dehydrogenated to 2-butanone. These reactions have also been

205   identified in other published studies on alcohol-promoted methanol synthesis [49].

206   Figure 3 depicts a typical concentration profile of the observed reaction products in 1-butanol during 6 hours of

207   reaction time. The temperature was 180 °C and pressure 60 bar for the experiment depicted. Similar concentration

208   curves were observed for all reaction conditions and alcohols used.
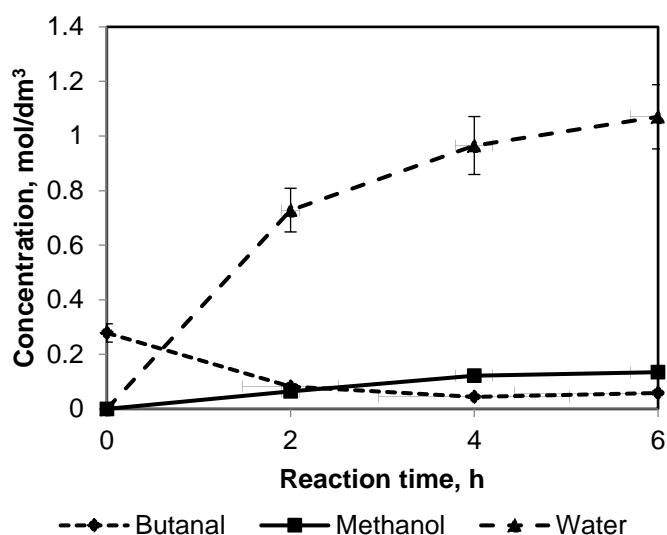
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210   **Figure 3.**   Typical concentration profile of the detected reaction products in 1-butanol. 20 g of Cu/ZnO catalyst

211   in 200 ml of alcohol, temperature 180 °C, feed gas $CO_2:H_2$ = 1:3, total pressure 60 bar.

212   The highest concentration of dehydrogenation products was found after heating of the reaction mixture prior to

213   introducing the reaction feed gas. A corresponding increase in the reactor pressure was noticed during the heating

214   process. The pressure increase was presumably caused by the hydrogen formed in the alcohol dehydrogenation

215   reaction. The peak concentration of the dehydrogenation products varied depending on the temperature and the

216   alcohol used but always remained below 10% of the total solution on a mass fraction basis. However, the

217   concentration of the aldehyde or ketone significantly decreased under the reaction gas atmosphere with increasing

218   reaction time. The dehydrogenation reactions appear to reverse direction under increased hydrogen pressure,

219 returning the original alcohols to the solution. Due to the relatively minor conversion of the alcohols and the apparent

220 reversibility of these reactions, alcohol dehydrogenation is not considered harmful for the overall process.

221 The concentration of methanol continuously increases over the 6 hours of reaction time. Thus, equilibrium

222 conversion is not reached during this time, and more methanol would likely form if the reaction time were increased.

223 The higher total concentrations of methanol and water found in the molecular sieve experiments (Section 3.3 Water

224 removal by molecular sieveare further evidence that the equilibrium product concentration is not reached. However,

225 in many of the experiments, the methanol production rate decreases after 4 hours of reaction time, as evidenced

226 by the declining slope of the methanol concentration curve in Figure 3. As the thermodynamic equilibrium is not

227 reached at this point, the methanol synthesis rate appears to be limited by kinetic effects, most likely by inhibition

228 caused by the by-product water.

229 The concentration of water also increases during the reaction as water is formed both as the by-product of CO_2

230 hydrogenation to methanol and also in the RWGS reaction. The amount of water formed is significantly higher than

231 the amount of methanol. In 1-butanol at 180 °C, the end concentration of water is almost 7 times the end

232 concentration of methanol (Figure 3). A similar result is found at higher reaction temperatures. Figure 4 presents

233 the concentrations of methanol and water in 1-butanol at reaction temperatures of 180, 200 and 220 °C.

234 If water is only formed as the by-product of methanol synthesis, the molar amounts of methanol and water formed

235 should be equal. The much higher concentrations of water compared to methanol suggest that a significant majority

236 of the water is formed in reactions other than methanol synthesis. On the Cu/ZnO catalyst, the RWGS reaction is

237 most likely the source of the excess water. The high molar ratios of water to methanol formed would suggest that

238 the RWGS reaction is the main reaction in this system and the total selectivity to methanol is rather low. In 1-butanol

239 (Figure 4), the molar ratio of water to methanol ranges approximately from 7 to 10, which implies methanol selectivity

240 in the range of 10-20 %. Some water is also present at the start of the reaction, most likely formed during the

241 reduction of the catalyst. This amount of water is significant in some of the experiments, for example, in 1-butanol

242 at 220 °C (Figure 4), constituting a potential disadvantage of the *in-situ* catalyst activation method.

243 Although hydrogenation of the esters is considered to be the rate-determining step in this process [26],

244 alkyl formates, the intermediate products of alcohol-promoted methanol synthesis, were not detected in

245 the reaction mixture, neither in 1-butanol nor in 2-butanol. The formate esters appear to be rapidly

246 hydrogenated into methanol and alcohol (reaction 9) and their concentrations remain below the detection

247 limit of the analysis method. As the intermediates were not detected, it was not possible to confirm that

248 the reactions proceed through the suggested reaction route. However, the overall promoting effect of the

249 alcohols was convincingly confirmed by a blank experiment in hexane at 180 °C, in which no methanol

250 was formed.
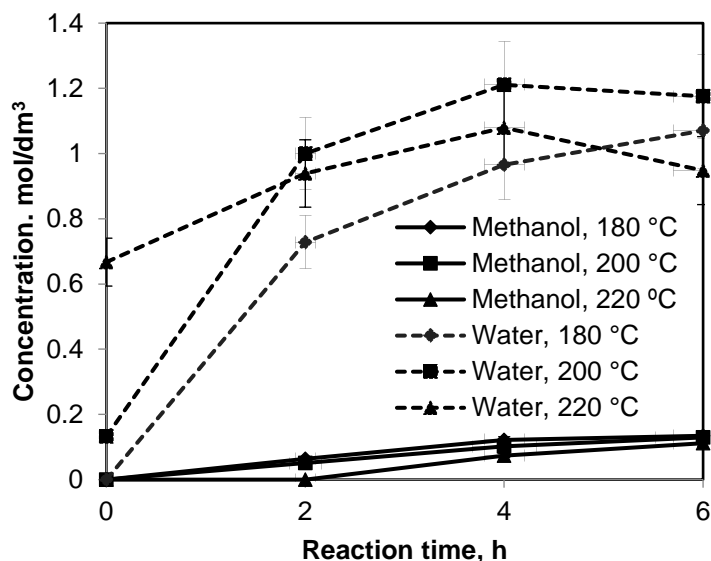
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252 **Figure 4.** Overall effect of temperature on the formation of methanol and water in alcohol promoted methanol

253 synthesis with 1-butanol as solvent. 20 g of Cu/ZnO catalyst. Feed gas CO_2:H_2 = 1:3. Total pressure

254 60 bar. Error bars for the concentration of water at 180 and 200 °C are omitted for clarity.

255 **3.2 Effect of reaction temperature and pressure**

256 Reactions in 1-butanol were carried out using a constant overall pressure at different temperatures. Figure 5 shows

257 the combined effect of the reaction temperature and the partial pressure of the reaction gas on methanol productivity

258 with constant total pressure at 180, 200 and 220 °C. The methanol productivity is measured as grams of methanol

259 produced per kg of catalyst per hour. The concentrations of the reaction products in these experiments are shown

260 in Figure 4. Methanol productivity is found to decrease with increasing temperature at the temperature range

261 studied. This result can be explained by the decreased partial pressure of the reaction gas due to increased vapor

262   pressure of 1-butanol at constant total pressure. The partial pressures, shown also in Figure 5, are calculated by

263   subtracting the alcohol vapor pressure from the total reaction pressure.

264
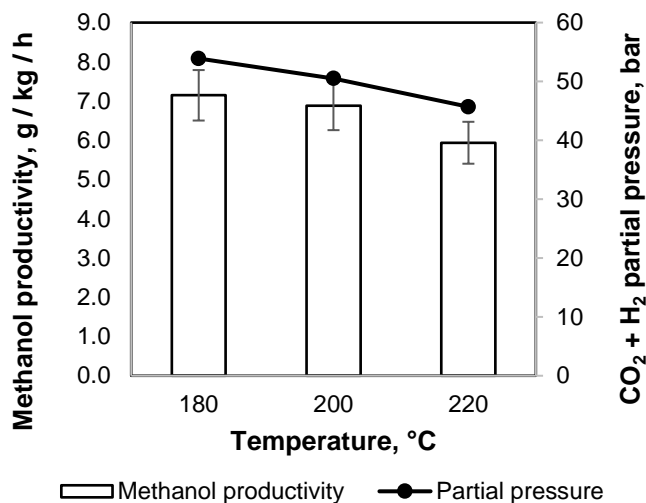
Figure 5.   Effect of temperature on methanol productivity with 20 g of Cu/ZnO catalyst in 200 ml of 1-butanol.

266   Reaction time 6 hours, feed gas CO_2:H_2 = 1:3, total pressure 60 bar.

267   As the concentration of water did not markedly change when the reaction temperature was varied (Figure 4), it can

268   be concluded that the effect of the RWGS reaction does not explain the lowered methanol productivity at increased

269   temperature.

270   In theory, the reduced methanol synthesis rate at increased temperatures could also be explained by increased

271   selectivity to CO. Increased CO formation by the RWGS reaction should also lead to increased production of water,

272   as water is also formed in the RWGS reaction. The increased concentrations of water would further inhibit the rate

273   of methanol synthesis. However, the concentration of water did not markedly change when the reaction temperature

274   was varied (Figure 4). Thus, it is concluded that the RWGS reaction does not explain the lowered methanol

275   productivity at increased temperature.

276   The reactions in 2-butanol were carried out using a constant reaction gas partial pressure at different temperatures

277   and a constant temperature at different reaction gas partial pressures. The effect of the feed gas partial pressure

278   on methanol productivity can be clearly seen in Figure 6, which presents methanol productivity at different reaction

279   temperatures with CO_2+H_2 partial pressure fixed to 40 bar by varying the total reaction pressure. A significant

280   increase in the methanol production rate with increasing reaction temperature is observed.

281   Figure 7 presents the methanol productivity at a fixed reaction temperature of 180 °C with the feed gas partial

282   pressure varied from 30 to 50 bar. The productivity clearly increases with the increased partial pressure. The

283   obtained productivities in 2-butanol seem to be higher than in 1-butanol. It should however be noted that the higher

284   productivity values in 2-butanol might be explained by the lower amount (10 g) of catalyst used. The specific

285   productivity of the catalyst appears to decrease as a result of increased water formation due to the RWGS reaction

286   when larger amounts of catalysts are used. This effect is discussed further in Section 3.3.
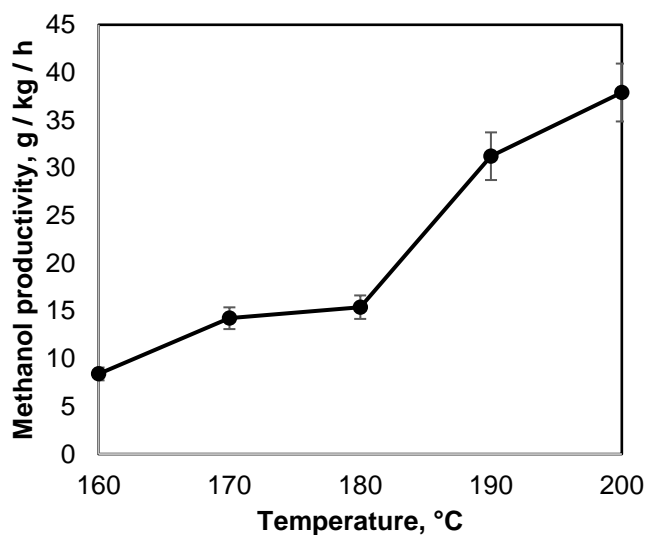
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288   **Figure 6.**   Effect of temperature on methanol productivity with 10 g of Cu/ZnO catalyst in 200 ml of 2-

289   butanol. Feed gas ($CO_2:H_2$ = 1:3), partial pressure 40 bar, reaction time 6 h.
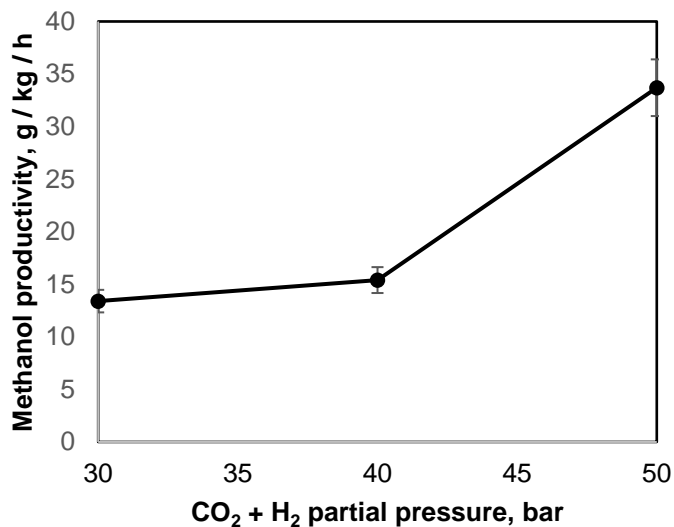
Figure 7. Effect of reaction gas partial pressure on methanol productivity with 10 g of Cu/ZnO catalyst in 2-butanol at 180 °C. Feed gas (CO_2:H_2 = 1:3), reaction time 6 h.

3.3 Water removal by molecular sieve

Continuous removal of water from the reaction mixture was tested by addition of a zeolite molecular sieve. Molecular sieves with a pore diameter of 3 Å can be used for the dehydration of alcohols because of their selective adsorption of water [50]. The selective adsorption is based on size exclusion of molecules larger than water in the inner microporous structure of the zeolite.

The limiting effect of water on the alcohol-promoted methanol synthesis process was first confirmed by performing an experiment with approximately 1.4 mol/dm^3 of water added to 2-butanol. This concentration is slightly above the maximum concentration range of water found in the experiments (Figure 4). At 180 °C and 60 bar of total pressure, the methanol production rate was approximately 74% lower than in the base experiment with no water added. The concentration of water did not significantly increase during this experiment but rather remained relatively constant at the apparent equilibrium level.

Next, the effect of *in-situ* adsorption of water by the addition of a 3Å molecular sieve was tested. The relative amounts of the catalyst and the molecular sieve were varied, maintaining a total solids mass of 50 g. The results of these experiments are presented in Figure 8. A base experiment with 20 g of catalyst and no molecular sieve is also presented for comparison.
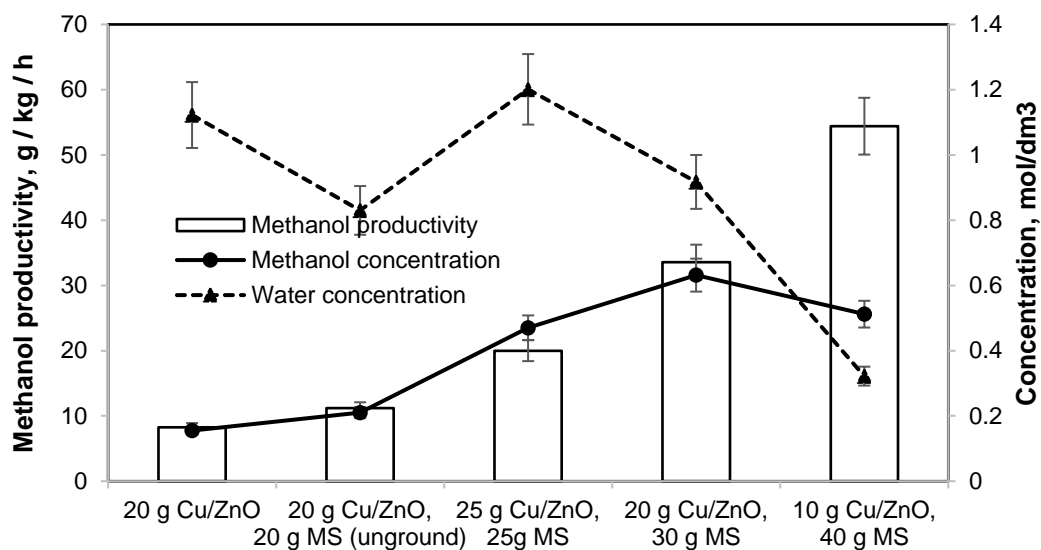
Figure 8. Effect of catalyst and molecular sieve mass on methanol and water formation in 2-butanol. Temperature 180 °C, feed gas CO_2:H_2 = 1:3, total pressure 60 bar.

Compared to the base case with 20 g of Cu/ZnO catalyst and no molecular sieve, the addition of the unground molecular sieve increased the methanol productivity from 8.2 g/kg/h to 11.2 g/kg/h. A more significant improvement was found with the molecular sieve ground into 150-300 µm particle size range. Due to the clear effect of the particle size, the adsorption of water appears to be significantly diffusion-limited for the unground molecular sieve. With 20 g of catalyst, the addition of 30 g of the ground molecular sieve increases the methanol productivity to 33.6 g/kg/h, an increase of over 300% over the Cu/ZnO catalyst used without a molecular sieve. Keeping the total amount of solids (catalyst + molecular sieve) at 50 g, the methanol productivity increased with increasing amounts of molecular sieve. For instance, the productivity increased to 54.4 g/kg/h using 10 g of the catalyst and 40 g of the molecular sieve. These results clearly show that the catalyst is most effectively utilized for methanol synthesis when larger relative amounts of the molecular sieve to the catalyst are used. This observation can be explained by the increased water adsorption capacity of the larger amount of the molecular sieve, leading to decreased concentrations of water, as shown in Figure 8.

324 **3.4 Dual catalysts**

325 To test the dual catalysis concept for alcohol-promoted methanol synthesis, copper chromite (CuCr) was used in

326 combination with the Cu/ZnO catalyst. The ratios of the two catalysts were varied: 20 g of the Cu/ZnO catalyst was

327 used with 10 g of CuCr, and vice versa. The experiments were carried out in 2-butanol at 180 °C and 60 bar of total

328 pressure, corresponding to a $CO_2 + H_2$ partial pressure of 50.1 bar. The results of these experiments are presented

329 in Figure 9. A base experiment with 20 g of Cu/ZnO catalyst and no copper chromite is also presented for

330 comparison.
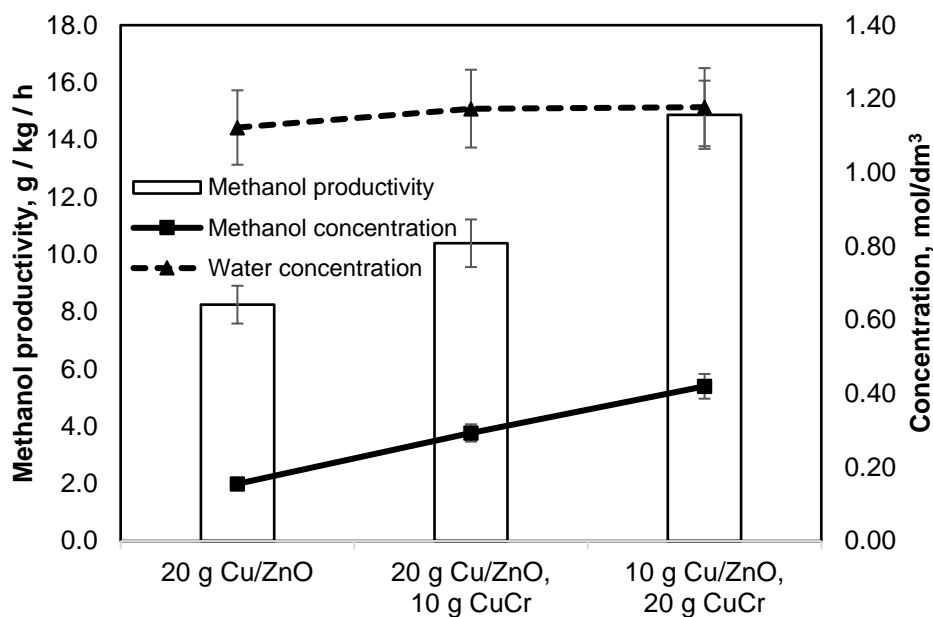
331

332 **Figure 9.** Effect of different amounts of Cu/ZnO and copper chromite (CuCr) catalysts on the formation of

333 methanol and water in 2-butanol. Reaction time 6 hours. Temperature 180 °C, feed gas $CO_2:H_2 =$

334 1:3, total pressure 60. An experiment with 20 g of Cu/ZnO catalyst and no copper chromite is

335 included for comparison.

336 The addition of the copper chromite catalyst clearly increases the methanol productivity. Both the absolute methanol

337 production rate, as measured by the methanol end concentration, and the specific productivity of the catalyst

338 increase with addition of copper chromite. The increased productivity can be explained either by a synergistic effect

339 between the two catalysts or by higher methanol synthesis activity of CuCr compared to Cu/ZnO. However, a higher

340 intrinsic activity of copper chromite appears unlikely, as the activity of Cu/ZnO for methanol synthesis is well-known

341 and industrially applied. Fan et al. [26] also reported higher methanol yield and selectivity of Cu/ZnO compared to

342 CuCr in alcohol promoted methanol synthesis. Fan et al. also found similar CO selectivity, or RWGS activity, for

343 both of the catalysts. This is supported by the present results, as the concentration of water was not significantly

344 affected by the changed ratio of Cu/ZnO and CuCr (Figure 9, columns 2 and 3), supporting similar RWGS activity

345 of the two catalysts. The overall methanol selectivity appears to be higher with the combined catalysts, as the ratio

346 of methanol to water produced is increased compared to Cu/ZnO used alone.

347 **3.5 Characterization of Cu/ZnO catalyst before and after reaction**

348 The structural features of the Cu/ZnO catalyst before and after reaction were investigated by the means

349 of XRD and SEM-EDS in order to assess the catalyst stability. Figure 10 presents the X-ray

350 diffractograms of the catalyst as supplied in the calcined form, following reduction in 5% hydrogen, and

351 following use in alcohol-promoted methanol synthesis in 1-butanol at 180 °C. It is noted that the same

352 batch of catalyst was analyzed prior to reduction and following the reaction, while the reduced catalyst

353 was prepared and analyzed separately.
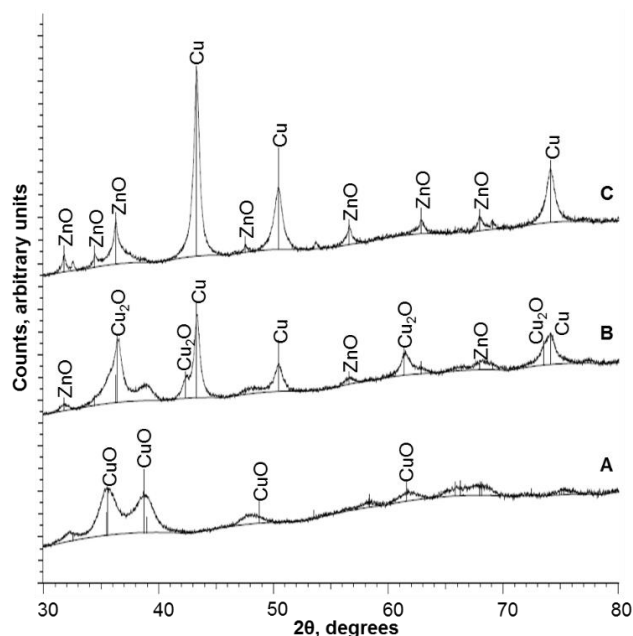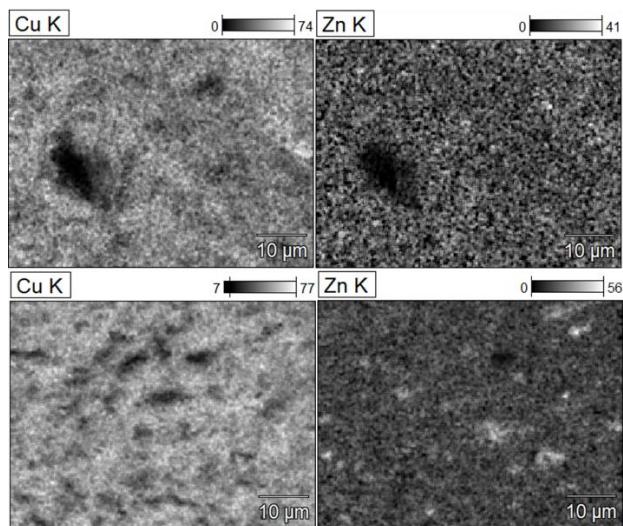

354

355 **Figure 10.**   X-ray diffractograms of the unused Cu/ZnO catalyst (A), the reduced catalyst (B), and the
356   catalyst following methanol synthesis from CO_2 and H_2 (1:3) in 1-butanol at 180 °C (C).

357   The calcined catalyst is largely amorphous, showing a minor pattern corresponding to copper(II)oxide

358   (CuO) typical to Cu/ZnO catalysts [51]. The patterns are identified based on the PDF 4+ 2018

359   crystallography database. The reduced catalyst presents with a clearly defined pattern consistent with

360   crystalline, copper(I)oxide (Cu_2O), and metallic copper. Weak crystalline features of zinc oxide are also

361   evident, consistent with previous studies [52]. As the reduction of copper proceeds stepwise from CuO

362   to Cu via Cu_2O [53], the presence of Cu_2O may imply incomplete reduction, possibly due to insufficient

363   reduction time or temperature. However, as the reduced catalyst sample was transferred and analyzed

364   in contact with air, re-oxidation of copper crystallites during this process cannot be ruled out.

365   Only metallic copper and zinc oxide is found present in the used catalyst. Cu/ZnO catalysts are known to

366   show dynamic structural changes depending on the oxidation potential of the gas phase [54, 55] and

367   ongoing reduction of the catalyst at the reaction conditions is possible. As the reduced and used catalyst

368   analyzed here are not from the same batch of ground and prepared catalyst, batch-to-batch variation

369   cannot be eliminated as a cause of the observed structural differences.

370   The peaks corresponding to zinc oxide are more clearly defined compared to the reduced catalyst,

371   potentially indicating continuing crystallization of ZnO at the reaction conditions. Lunkenbein et al. [56]

372   identified zinc oxide as the more dynamic phase compared to metallic copper under reaction conditions,

373   and found that crystallization of ZnO and the resulting loss of reactive Cu-ZnO interfaces is the main

374   mechanism of initial catalyst deactivation. The SEM-EDS elemental maps of copper and zinc presented

375   in Figure 11 indicate that such a process may have initiated in the catalyst used here. The unused

376   (calcined) catalyst shows a relatively homogeneous distribution of both copper and zinc. However, a

377   degree of segregation of these elements can be observed in the used catalyst, with the elemental map

378   showing distinct areas with high content of zinc (oxide) that are relatively poor in copper.

Figure 11. SEM-EDS elemental maps of copper and zinc in the unused Cu/ZnO catalyst (upper), and the catalyst following methanol synthesis from CO_2 and H_2 (1:3) in 1-butanol at 180 °C (lower). Composition scales in weight percent.

Further insight is provided by the SEM images presented in Figure 12. Distinct crystals in the micrometer dimension can be observed, identified as zinc oxide by the EDS analysis. No such features were found in the unused catalyst. It is concluded that agglomeration and crystallization of zinc oxide during reaction has occurred, acting as a potential deactivation mechanism for the catalyst. However, as long-term stability tests were not performed here, the actual effect of these structural changes on the activity of the catalyst cannot be discussed.

These observations can be compared to other findings discussed in literature. Previously, the stability of Cu/ZnO catalyst in alcohol promoted methanol synthesis has been explored by Reubroycharoen et al. [32] who found the performance stable during 40 hours of continuous methanol synthesis (at 170 °C), and by Jeong et al. [57] who found no decline in activity during 60 hours of reaction (150 °C). In contrast to our results, Jeong et al. found no changes in the XRD profile of the catalyst before and after reaction. Other than the lower reaction temperature, the differing findings might be explained by different feed gas composition, as a CO-rich syngas was used in these studies opposed to the CO_2:H_2

397 mixture used here. Therefore, it is possible that the detected differences might be caused by the large

398 amount of water present in the reaction system in the present study.

399

400 **Figure 12.**   SEM micrographs of the Cu/ZnO catalyst following methanol synthesis from CO_2 and H_2
401 (1:3) in 1-butanol at 180 °C. Zinc oxide crystals are highlighted.

402 **4. Conclusions**

403 Methanol synthesis from CO_2 was studied in an alcohol-promoted liquid-phase process using conventional Cu/ZnO

404 and copper chromite as catalysts. 1-butanol and 2-butanol were found to act as catalytic solvents, allowing methanol

405 synthesis at lower temperatures than conventional gas-phase processes. Although it was not possible to determine

406 the exact reaction route, it is expected that the promoting effect of the alcohols is based on a reaction route

407 proceeding through the intermediate of formate ester of the alcohol.

408 The effect of continuous water removal using molecular sieve adsorption was explored. The addition of a 3Å

409 molecular sieve significantly enhanced methanol productivity. Grinding of the molecular sieve resulted in improved

410 results due to the shorter diffusion path compared to the granular material. The maximum methanol productivity of

411 54.4 g/kg/h was found when the maximum relative amount of the molecular sieve (40 g) to the catalyst (10 g) was

412 used. The final methanol concentration after 6 hours of reaction time reached 0.5 mol/dm^3. The catalyst was most

413 effectively used for methanol synthesis when the amount of molecular sieve was maximized, which minimized the

414 concentration of water. The water concentration was found to significantly affect the rate of methanol synthesis.

415 The overall methanol production rate in this process appears to be limited by the concentration of water and its

416 effects on the catalyst surface. To prevent the negative effects of water, continuous water removal or development

417 of more water resistant catalysts is vital for further development of this process. Based on the results, the use of a

418 3Å molecular sieve for water removal appears a promising approach.

419 The methanol productivity obtained in the current research can be compared to results reported in other studies.

420 Yang et al. [49] found an even higher methanol productivity of up to 167 g/kg/h for alcohol-promoted methanol

421 synthesis at 170 °C and 50 bar using an optimized Cu/ZnO catalyst composition. The difference to the results

422 presented here can be explained mainly by the different feed gas composition in their experiments (CO/CO$_2$/H$_2$/Ar

423 = 32.4/5.1/59.5/3.9). For gas-phase CO$_2$ hydrogenation to methanol, productivity values even up to 1200 g/kg/h

424 have been achieved [58]. However, these results were obtained at a relatively high temperature of 240 °C and at

425 high space velocities giving relatively low CO$_2$ conversions.

426 Dual catalysis by the combination of Cu/ZnO with copper chromite was also studied in this work. A remarkable

427 increase in catalytic activity was found for the dual catalyst. When 20 g of copper chromite and 10 g of Cu/ZnO was

428 used, the productivity increased by 80% compared to the use of 20 g of the Cu/ZnO catalyst alone. A synergistic

429 effect between the two catalysts is suggested, which is possibly based on an increased formation rate of the formate

430 ester intermediate by the copper chromite catalyst. The two catalysts appeared to have similar reverse water-gas

431 shift activity, as the concentration of water did not change when the relative amounts of Cu/ZnO and copper chromite

432 were varied.

433 Structural changes in the catalyst during alcohol-promoted methanol synthesis were found by the means of XRD

434 and SEM-EDS investigations. EDS elemental analysis showed that segregation of copper and zinc oxide had taken

435 place, and both XRD analysis and SEM imaging provided evidence that crystallization of zinc oxide occurred. Such

436 phenomena has previously been identified as cause of catalyst deactivation due to the loss of reactive Cu-ZnO

437 interfaces [56]. However, comprehensive catalyst stability tests were not performed in the current study, and thus

438   the effect of the observed changes on catalytic activity cannot be determined conclusively. It is clear that stability

439   tests at different reaction temperatures and, importantly, at different feed gas compositions are necessary to further

440   characterize the alcohol-promoted methanol synthesis process.

441   **Acknowledgements**

445 **References**

[1] R. Schlögl, "The solar refinery," in *Chemical Energy Storage*, Berlin/Boston, Walter de Gruyter GmbH, 2013, pp. 1-34.

[2] F. Schüth, "Energy storage strategies," in *Chemical Enery Storage*, Berlin/Boston, Walter de Gruyter GmbH, 2013, pp. 35-48.

[3] G. Olah, "Beyond oil and gas: The methanol economy," *Angew. Chem. Int. Ed.,* vol. 44, pp. 2636-2639, 2005. doi:10.1002/anie.200462121

[4] H. Offermanns, L. Plass and M. Bertau, "From raw materials to methanol, chemicals, and fuels" in *Methanol: The Basic Chemical and Energy Feedstock of the Future*, Berlin Heidelberg, Springer-Verlag, 2014, pp. 1-7. doi:10.1007/978-3-642-39709-7

[5] L. Reichelt and F. Schmidt, "Methanol-to-gasoline process," in *Methanol: The Basic Chemical and Energy Feedstock of the Future*, Berlin Heidelberg, Springer-Verlag, 2015, pp. 440-453. doi:10.1007/978-3-642-39709-7

[6] F. Schmidt and C. Pätzold, "Methanol-to-olefins processes," in *Methanol: The Basic Chemical and Energy Feedstock of the Future*, Berlin Heidelberg, Springer-Verlag, 2015, pp. 454-472. doi:10.1007/978-3-642-39709-7

[7] J. Ott, V. Gronemann, F. Pontzen, E. Fiedler, G. Grossmann, Kersebohm, D.B., G. Weiss and C. Witte, "Methanol," in *Ullmann's Encyclopedia of Industrial Chemistry*, Weinheim, Wiley-VCH Verlag GmbH & Co. KGaA, 2012, pp. 1-27. doi:10.1002/14356007

[8] S. Lee, "Methanol synthesis from syngas," in *Handbook of Alternative Fuel Technology*, Taylor & Francis Group, LLC, 2007, pp. 297-321.

[9] J. Skrzypek, M. Lachowska, M. Grzesik, J. Sloczynski and P. Nowak, "Thermodynamics and kinetics of low pressure methanol synthesis," *Chem. Eng. J.,* vol. 58, pp. 101-108, 1995. doi:10.1016/0923-0467(94)02955-5

[10] E. Kunkes and M. Behrens, "Introduction to methanol synthesis and steam reforming," in *Chemical Energy Storage*, Berlin, Walter de Gruyter GmbH, 2013, pp. 415-417.

[11] T. Holderbaum and J. Gmehling, "PSRK: A group contribution equation of state based on UNIFAC," *Fluid Phase Equilib.,* vol. 70, pp. 251-265, 1991. doi:10.1016/0378-3812(91)85038-V

[12] V. Palekar, "Alkali compounds and copper chromite as low-temperature slurry phase methanol catalysts," *Appl. Catal., A,* vol. 103, no. 1, pp. 105-122, 1993. doi:10.1016/0926-860X(93)85177-Q

[13] Y. Zhao, L. Bai, Y. Hu, B. Zhong and S. Peng, "Catalytic performance of $CuCr/CH_3ONa$ used for low temperature methanol synthesis in slurry phase," *J. Nat. Gas Chem.,* vol. 8, no. 3, pp. 181-187, 1999.

[14] W. Chu, T. Zhang, C. He and Y. Wu, "Low-temperature methanol synthesis (LTMS) in liquid phase on novel copper-based catalysts," *Catal. Lett.,* vol. 79, pp. 129-132, 2002. doi:10.1023/A:1015384015528

[15] M. Marchionna, L. Basini, A. L. M. Aragno and F. Ancillotti, "Mechanistic studies on the homogeneous nickel-catalyzed low temperature methanol synthesis," *J. Mol. Catal.,* vol. 75, no. 2, pp. 147-151, 1992. doi:10.1016/0304-5102(92)80116-X

[16] E. Lee and K. Aika, "Low-temperature methanol synthesis in liquid-phase with a Raney Nickel–alkoxide system: Effect of Raney Nickel pretreatment and reaction conditions," *J. Mol. Catal. A: Chem.,* vol. 141, pp. 241-248, 1999. doi:10.1016/S1381-1169(98)00267-2

[17] S. Ohyama, "Low-temperature methanol synthesis in catalytic systems composed of nickel compounds and alkali alkoxides in liquid phases," *Appl. Catal. A,* vol. 180, pp. 217-225, 1999. doi:10.1016/S0926-860X(98)00338-X

[18] V. Palekar, H. Jung, J. Tierney and I. Wender, "Slurry phase synthesis of methanol with a potassium methoxide/copper chromite catalytic system," *Appl. Catal. A,* vol. 102, no. 1, pp. 13-34, 1993. doi:10.1016/0926-860X(93)85152-F

[19] R. Sapienza, W. Slegeir, T. O'Hare and D. Mahajn, "Low temperature catalysts for methanol production". United States of America Patent US4614749A, 30 September 1986.

[20] S. Lee and A. Sardesai, "Liquid phase methanol and dimethyl ether synthesis from syngas," *Top. Catal.,* vol. 32, pp. 197-207, 2005. doi:10.1007/s11244-005-2891-8

[21] G. Chinchen, P. Denny, D. Parker, M. Spencer and D. Whan, "Mechanism of methanol synthesis from $CO_2/CO/H_2$ mixtures over copper/zinc oxide/alumina catalysts: use of 14C-labelled reactants," *Appl. Catal.,* vol. 30, no. 2, pp. 333-338, 1987. doi:10.1016/S0166-9834(00)84123-8

[22] G. Olah, A. Goeppert and G. Surya Prakash, "Chemical recycling of carbon dioxide to methanol and dimethyl ether: From greenhouse gas to renewable, environmentally carbon neutral fuels and synthetic hydrocarbons," *J. Org. Chem.,* vol. 74, pp. 487-498, 2009. doi:10.1021/jo801260f

[23] O. Joo, K. Jung, I. Moon, A. Rozovskii, G. Lin, S. Han and S. Uhm, "Carbon dioxide hydrogenation to form methanol via a reverse-water-gas-shift reaction (the CAMERE Process)," *Ind. Eng. Chem. Res.,* vol. 38, pp. 1808-1812, 1999. doi:10.1021/ie9806848

[24] J. Tremblay, "CO_2 as feedstock," *Chem. Eng. News,* vol. 86, p. 13, 2008.

[25] Carbon Recycling International, "World's largest CO_2 methanol plant," [Online]. Available: http://carbonrecycling.is/george-olah/. [Accessed 16 August 2017].

[26] L. Fan, Y. Sakaiya and K. Fujimoto, "Low-temperature methanol synthesis from carbon dioxide and hydrogen via formic ester," *Appl. Catal. A,* vol. 180, pp. L11-L13, 1999. doi:10.1016/S0926-860X(98)00345-7

[27] B. Xu, R. Yang, F. Meng, P. Reubroucharoen, T. Vitidsant, Y. Zhang, Y. Yoneyama and N. Tsubaki, "A new method of low temperature methanol synthesis," *Catal. Surv. Asia,* vol. 13, pp. 147-163, 2009. doi:10.1007/s10563-009-9075-7

[28] R. Yang, Y. Fu, Y. Zhang and N. Tsubaki, "In situ DRIFT study of low-temperature methanol synthesis mechanism on Cu/ZnO catalysts from CO_2-containing syngas using ethanol promoter," *J. Catal.,* vol. 228, no. 1, pp. 23-35, 2004. doi:10.1016/j.jcat.2004.08.017

[29] R. Yang, Y. Zhang and N. Tsubaki, "Dual catalysis mechanism of alcohol solvent and Cu catalyst for a new methanol synthesis method," *Catal. Commun.,* vol. 6, no. 4, pp. 275-279, 2005. doi:10.1016/j.catcom.2005.01.008

[30] N. Tsubaki, M. Ito and K. Fujimoto, " A new method of low-temperature methanol synthesis," *J. Catal.,* vol. 197, pp. 224-227, 2001. doi:10.1006/jcat.2000.3077

[31] J. Zeng, K. Fujimoto and N. Tsubaki, "A new low-temperature synthesis route of methanol: Catalytic effect of the alcoholic solvent," *Energy Fuels,* vol. 16, pp. 83-86, 2002. doi:10.1021/ef0100395

[32] P. Reubroycharoen, T. Yamagami, T. Vitidsant, Y. Yoneyama, M. Ito and N. Tsubaki, "Continuous low-temperature methanol synthesis from syngas using alcohol promoters," *Energy Fuels,* vol. 17, pp. 817-823, 2003. doi:10.1021/ef020240v

[33] C. Huff and M. Sanford, "Cascade catalysis for the homogeneous hydrogenation of CO_2 to methanol," *J. Am. Chem. Soc.,* vol. 133, pp. 18122-18125, 2011. doi:10.1021/ja208760j

[34] Y. Chen, S. Choi and L. Thompson, "Low-temperature CO_2 hydrogenation to liquid products via a heterogeneous cascade catalytic system," *ACS Catal.,* vol. 5, pp. 1717-1725, 2015. doi:10.1021/cs501656x

[35] T. Turek and D. Trimm, "The catalytic hydrogenolysis of esters to alcohols," *Catal. Rev.: Sci. Eng.,* vol. 36, pp. 645-683, 1994. doi:10.1080/01614949408013931

[36]   M. Sahibzada, I. S. Metcalfe and D. Chadwick, "Methanol synthesis from $CO/CO_2/H_2$ over Cu/ZnO/Al2O3 at differential and finite conversions," *J. Catal.,* vol. 174, pp. 111-118, 1998. doi:10.1006/jcat.1998.1964

[37]   O. Martin and J. Pérez-Ramírez, "New and revisited insights into the promotion of methanol synthesis catalysts by CO_2," *Catal. Sci. Technol.,* vol. 3, pp. 3343-3352, 2013. doi:10.1039/C3CY00573A

[38]   R. Struis, S. Stucki and M. Wiedorn, "A membrane reactor for methanol synthesis," *J. Membr. Sci.,* vol. 113, pp. 93-100, 1996. doi:10.1016/0376-7388(95)00222-7

[39]   F. Gallucci, L. Paturzo and A. Basile, "An experimental study of CO_2 hydrogenation into methanol involving a zeolite membrane reactor," *Chem. Eng. Process.,* vol. 43, pp. 1029-1036, 2004. doi:10.1016/j.cep.2003.10.005

[40]   J. van Bennekom, R. Venderbosch, J. Winkelman, E. Wilbers, D. Assink, K. Lemmens and H. Heeres, "Methanol synthesis beyond chemical equilibrium," *Chem. Eng. Sci.,* vol. 87, pp. 204-208, 2013. doi:10.1016/j.ces.2012.10.013

[41]   M. Bos And D. Brilman, "A novel condensation reactor for efficient CO2 to methanol conversion for storage of renewable electric energy," *Chem. Eng. J.,* vol. 278, pp. 572-532, 2015. doi:10.1016/j.cej.2014.10.059

[42]   M. Malone and M. Doherty, "Reactive distillation," *Ind. Eng. Chem. Res.,* vol. 39, pp. 3953-3957, 2000. doi:10.1021/ie000633m

[43]   J. Allison, H. Wright, T. Harkins and D. Jack, "Use of catalytic distillation reactor for methanol synthesis". United States of America Patent US 6,723,886 B2, 20 April 2004.

[44]   S. Srinivas, R. Malik and S. Mahajani, "Feasibility of reactive distillation for Fischer−Tropsch synthesis," *Ind. Eng. Chem. Res.,* vol. 47, pp. 889-899, 2008. doi:10.1021/ie071094p

[45]   M. Bayat, Z. Dehghani, M. Hamidi and M. Rahimpour, "Methanol synthesis via sorption-enhanced reaction process: Modeling and multi-objective optimization," *J. Taiwan Inst. Chem. Eng.,* vol. 45, no. 2, pp. 481-494, 2014. doi:10.1016/j.jtice.2013.06.013

[46]   I. Illiuta, M. Illiuta and F. Larachi, "Sorption-enhanced dimethyl ether synthesis—Multiscale reactor modeling," *Chem. Eng. Sci.,* vol. 66, no. 10, pp. 2241-2251, 2011. doi:10.1016/j.ces.2011.02.047

[47]   J. Keuler, L. Lorenzen and S. Miachon, "The dehydrogenation of 2-butanol over copper-based catalysts: optimising catalyst composition and determining kinetic parameters," *Appl. Catal., A,* vol. 218, pp. 171-180, 2001. doi:10.1016/S0926-860X(01)00639-1

[48]   S. Mostafa, J. Croy, H. Heinrich and B. Roldan Cuenya, "Catalytic decomposition of alcohols over size-selected Pt nanoparticles supported on ZrO_2: A study of activity, selectivity, and stability," *Appl. Catal., A,* vol. 366, pp. 353-362, 2009. doi:10.1016/j.apcata.2009.07.028

[49]   R. Yang, X. Yu, Y. Zhang, W. Li and N. Tsubaki, "A new method of low-temperature methanol synthesis on $Cu/ZnO/Al_2O_3$ catalysts from $CO/CO_2/H_2$," *Fuel,* vol. 87, pp. 443-450, 2008. doi:10.1016/j.fuel.2007.06.020

[50]   N. Tsubaki, J. Zeng, Y. Yoneyama and K. Fujimoto, "Continuous synthesis process of methanol at low temperature from syngas using alcohol promoters," *Catal. Commun.,* vol. 2, pp. 213-217, 2001. doi:10.1016/S1566-7367(01)00039-5

[51]   W. Teo and D. Ruthven, "Adsorption of water from aqueous ethanol using 3-Å molecular sieves," *Ind. Eng: Chem. Process Des. Dev.,* vol. 25, no. 1, pp. 17-21, 1986. doi:10.1021/i200032a003

[52]   T. Kandemir, F. Girgsdies, T. Hansen, K. Liss, I. Kasatkin, E. Kunkes, G. Wowsnick, N. Jacobsen, R. Sclögl, and M. Behrens, "In Situ Study of Catalytic Processes: Neutron Diffraction of a Methanol Synthesis Catalyst at Industrially Relevant Pressure," *Angew. Chem. Int. Ed.*, vol. 52, pp. 5166-5170, 2013

[53] J. Sloczynski, R. Grabowski, A. Kozłowska, P. K. Olszewski and J. Stoch, "Reduction kinetics of CuO in CuO/ZnO/ZrO$_2$ systems," *Phys. Chem. Chem. Phys.*, vol. 5, pp. 4631-4640, 2003. doi:10.1039/b306132a

[54] J. Grunwaldt, A. Molenbroek, N. Topsøe, H. Topsøe, and B. Clausen, "In Situ Investigations of Structural Changes in Cu/ZnO Catalysts," *J. Catal.*, vol. 194, pp. 452-460. 2000. doi:10.1006/jcat.2000.2930

[55] P. Hansen, J. Wagner, S. Helveg, J. Rostrup-Nielsen, B. Clausen and H. Topsøe, "Atom-Resolved Imaging of Dynamic Shape Changes in Supported Copper Nanocrystals," *Science*, vol. 295, pp. 2053-2055, 2002 doi:10.1126/science.1069325

[56] T. Lunkenbein, F. Girgsdies, T. Kandemir, N. Thomas, M. Behrens, R. Schlögl and E. Frei, "Bridging the Time Gap: A Copper/Zinc Oxide/Aluminum Oxide Catalyst for Methanol Synthesis Studied under Industrially Relevant Conditions and Time Scales," *Angew. Chem.*, vol. 128, pp. 12900-12904, 2016 doi:10.1002/anie.201603368

[57] Y. Jeong, I. Kim, J. Kang, H. Jeong, J. Park, J. Park and J. Jung, "Alcohol-assisted low temperature methanol synthesis from syngas over Cu/ZnO catalysts: Effect of pH value in the co-precipitation step," *J. Mol. Catal. A: Chem.*, vol. 400, pp. 132-138, 2015 doi:10.1016/j.molcata.2015.01.008

[58] F. Arena, G. Mezzatesta, G. Zafarana, G. Trunfio, F. Frusteri and L. Spadaro, "Effects of oxide carriers on surface functionality and process performance of the Cu–ZnO system in the synthesis of methanol via CO$_2$ hydrogenation," *J. Catal.,* vol. 300, pp. 141-151, 2013. doi:10.1016/j.jcat.2012.12.019

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